Abstract

Fluid transport in pores of molecular dimension is frequently encountered in various applications such as chromatography, oil recovery, gas storage, membrane separation technologies and catalytic chemical reactions. Under nanoscale confinement, interactions of the fluid molecules with the pore walls alter the structural as well as dynamic properties of the confined fluid in comparison to bulk fluids. Confined fluid behaviour has been studied in nanopores such as zeolites and graphitic slit pores Carbon nanotubes (CNTs) with their hollow cylindrical shape and large surface area are potential candidates for novel gas storage devices and membrane separation technologies In this thesis we are concerned with obtaining an understanding of dynamics of fluids confined in CNTs

Although molecular dynamics (MD) simulations have been used to obtain time correlation functions and transport properties of confined fluids, there have been relatively few attempts to model the dynamics and velocity auto correlation function (VACF) of confined fluids Most of the theoretical approaches have been successful for the short time dynamics of the fluid These include methods based on short time expansions, memory kernel methods and those based on instantaneous normal modes The intermediate and long time dynamics where collective effects are important have been approached using mode coupling theories

In this thesis we have modelled the power spectrum of VACF also known as the density of states for Argon confined in a single wall carbon nanotube (SWNT) over a range of pore densities and temperatures. This approach directly yields the VACF and self-diffusivity of the confined fluid The method tested in this thesis is based on a recent model for the power spectrum involving gamma distributions, where the gamma model was shown to yield excellent results for the dynamics of bulk liquids and fluids confined in slit shaped pores The inputs into the model are the frequency moments.

Our study indicates that the method is able to capture the dominant features in the power spectrum as a function of density and temperature in SWNT (16,16) In general

the model is seen to predict qualitative trends in the self-diffusivity as a function of pore density and temperature for all the state points investigated

The last Chapter in this thesis is concerned with transport of mixtures in carbon nanotubes, where we investigate the contribution of distinct diffusivity to the overall mutual diffusivity in the mixtures In the frame work of equilibrium MD simulations, the mutual diffusivity D_{11} contains contributions from the self diffusivity D_s and the distinct diffusivity D_d

$$D_{11} = D_s + D_d$$

D_s has contribution from the VACFs of the individual species The distinct diffusivity D_d on the other hand has contribution from the velocity cross correlation functions D_d can be either negative or positive In order to asses the contribution of D_d in D_{11} relative to self-diffusivity D_s, a ratio R is defined as

$$R = \frac{D_{11}}{D_s}$$

For mixtures with a value of R close to unity, the contribution from D_d is small relative to the contribution from D_s The ratio R have been evaluated in the barycentric reference frame for three different binary mixtures The first one (M_1) represent an Ar-Kr mixture. The second mixture (M_2) corresponds to Ar-Xe and the third mixture (M_3) has similar energy and mass ratios as the Ar-Xe mixture with $\mu = 1$, where $\mu = \sigma_{22}/\sigma_{11}$, σ_{11} and σ_{22} are the Lennard-Jones diameters of the species-1 and 2 in mixture

From the values of R obtained in this study, it is clear that R is close to unity for all the mixtures examined A similar conclusion was reached in an earlier study of rare gas mixtures in slit graphite pores A knowledge of the magnitude of D_d relative to D_s as reflected in the ratio R facilitates evaluating the transport flux for confined mixtures If D_d is small as illustrated in this and earlier studies, mutual diffusivities can easily be evaluated with a knowledge of the self-diffusivities. Since self-diffusivities can be obtained accurately from equilibrium molecular dynamics simulations, time intensive non-equilibrium simulations can be avoided to compute the mutual diffusivity